

Spin-Boson Theory for Magnetotransport in Organic Semiconducting Materials

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We present a spin-boson theory for magnetotransport in organic semiconducting materials, on the basis of a coupling between charge carriers' spin and a local bosonic environment, which is shown to be an irreducible ingredient in understanding of the anomalous organic magnetoresistance (OMR). Among those composing this environment triplet-excitons play a basic role. The incoherent hopping rate between molecules is calculated to give out the fundamental behavior of OMR. The underlying mechanism is revealed from the calculation of entanglement, represented by the von Neumann entropy, between the carrier's spin and bosons. We also obtain the dependence of OMR on the bias voltage, the spin-boson coupling, and the boson frequency. The results obtained from the theory are in good agreement with experiments.

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The discovery of room-temperature, low-field magnetoresistance (MR) in organic light-emitting devices (OLEDs) was one of the major achievements of spintronics in the last decade.[1, 2] Compared to its inorganic counterparts, a sizable organic MR (OMR) is relatively easy to be obtained, showing extensive potential in magnetically controlled applications.[3] Yet, after years of intense research, the origin of this magnetic field effect out of these nonmagnetic materials remains controversial. Traditional theories of MR in inorganic materials, such as that based on Lorentz force or spin-orbit coupling, are recognized to be invalid in organic materials.[4] The hyperfine interaction (HFI) caused by hydrogen nuclei in organic molecules has been thought to be significant,[5] which is verified very recently by an experiment on isotope effect in spin response of π -conjugated polymers.[6] Meanwhile, a similar experiment in the Alq_3 showed the response is isotope independent,[7] which seems interactions other than HFI may dominate the spin process. A bipolaron model[8] using Monte Carlo (MC) simulation gave a mechanism for both of positive and negative OMR at high density of charge carriers. The MC method has also been successfully extended to study spin diffusion in spin valve effect based on incoherent hopping of a charge carrier and coherent precession of its spin.[9] Moreover, there are experiments indicating that the behavior of OMR at low field might be different with that at relatively high field.[3, 10] In a word, a comprehensive understanding of the experimental phenomena will be enlightening.

A proper theory that describes the intrinsic physics of OMR should incorporate the following considerations: (i) A prominent characteristic of charge transport in organic semiconducting materials is the incoherent hopping between molecules;[11] (ii) The spin decoherence time is about $0.5\mu\text{s}$,[12] much longer than the time ($\sim 100\text{ns}$ in Alq_3) for carriers transporting in devices.[13] Further, the intermolecular hopping was observed to be spin-conserving,[14] which implies the motion of carriers'

spin is coherent;[9] (iii) The OMR is robust under room temperature.[15] Even though the Zeeman splitting energy of about 100mT is much smaller than the thermal energy, the effect of magnetic field will not be smeared out by the thermal fluctuation, for the motion of spins being coherent in the whole process. For the same reason, the effect is little influenced by all other things that are not interacting with spins; (iv) There are contradictions among various experiments on the role of excitons. On one hand, these processes associated with excitons, such as intersystem crossing between singlet and triplet excitons[3, 16], and triplet-triplet annihilation[17, 18] were regarded as the main response to magnetic field, which implies the role is essential. This might be complemented by a recent experiment of transient electroluminescence, which revealed that OMR could be observed only when the carriers and excitons coexist in the system.[19] On the other hand, there are also evidences that the excitons are irrelevant to the OMR, for example, the measurement of the intersystem crossing rate shows it is magnetic field independent.[14, 20] As a result, it can be realized from above that all mentioned mechanisms overlook the scattering of carriers from excitons, which should be a *primary* role of excitons in the magnetotransport.

With those considerations, we propose a spin-boson theory for magnetotransport in this Letter. The Hamiltonian we suggest for the theory is expressed as

$$H = \sum_n H_n + H', \quad (1)$$

where the intramolecular part of the n -th molecule

$$H_n = \sum_{\alpha} [\hbar\omega_{n,\alpha} b_{n,\alpha}^{\dagger} b_{n,\alpha} + \gamma_{n,\alpha} (b_{n,\alpha}^{\dagger} + b_{n,\alpha}) S_n^z] + g\mu_B \mathbf{B} \cdot \mathbf{S}_n \quad (2)$$

describes the spin interaction of a charge carrier with a local bosonic environment in an external magnetic field \mathbf{B} . Here, \mathbf{S}_n (S_n^z) is the (z -direction) spin operator of a

carrier, $b_{n,\alpha}^\dagger$ ($b_{n,\alpha}$) creates (annihilates) a boson that is the α -th mode of the environment, $\omega_{n,\alpha}$ the corresponding frequency of bosons, $\gamma_{n,\alpha}$ the spin-boson coupling, g the Landé factor that is set to be the commonly accepted value 2.0, μ_B the Bohr magneton, and z direction is chosen along that of the specific bosonic mode at each molecule. As an important characteristic of organic materials, when a carrier hops into a molecule, it is immersing in a complex and disordered surrounding medium. This medium could be treated as an environment composed of a number of bosons.[21] Many factors contribute to the medium, such as local molecular vibration modes, hydrogen nuclear spin, and excitons, in a way that depends on materials.[6] Especially, triplet excitons should play a basic role for their long lifetime and weak diffusive ability compared with that of charge carriers.[22] The environment could be regarded to be an effective magnetic field defined as

$$B_{0n} = \frac{1}{g\mu_B} \sum_{\alpha} \gamma_{n,\alpha} \langle b_{n,\alpha}^\dagger + b_{n,\alpha} \rangle \quad (3)$$

to the carriers' spin plus quantum fluctuation that will be shown to be crucial to give the magnetic field effect. The intermolecular part of (1)

$$H' = \sum_{n,n',\sigma} J_{nn'} (c_{n,\sigma}^\dagger c_{n',\sigma} + \text{h.c.}) \quad (4)$$

describes the carrier's hopping between molecules. $c_{n(n'),\sigma}^\dagger$ ($c_{n(n'),\sigma}$) creates (annihilates) a carrier with spin σ at $n(n')$ -th molecule, and $J_{nn'}$ the overlap integral of wavefunctions between molecules. This term includes all the magnetism independent factors in conventional treatment of organic charge transport, such as disorders of molecular energies and intermolecular distances, which ensures that we could only consider a spin-related Hamiltonian for H_n .

Considering the characteristic of organic materials as discussed above, we could write the density matrix of the system as a direct sum of all local density matrices of molecules, that is,

$$\rho = \rho_1 \oplus \rho_2 \oplus \cdots \rho_n \oplus \cdots, \quad (5)$$

and divide the whole process into two steps, intramolecular evolution and intermolecular hopping, to calculate the incoherent hopping rate of a single charge carrier. The dynamical evolution follows the equation of motion,

$$i\hbar \frac{\partial}{\partial t} \rho_n = [H_n, \rho_n]. \quad (6)$$

H_n could be numerically diagonalized by constructing the following basis, indexed by a set of integer numbers $\{l_\alpha\}$, [23]

$$|\{l_\alpha\}, s\rangle = \prod_{\alpha} \frac{e^{-u_\alpha^2/2}}{\sqrt{l_\alpha!}} (\hat{b}_\alpha^\dagger + su_\alpha)^{l_\alpha} e^{-su_\alpha \hat{b}_\alpha^\dagger} |\{0\}, s\rangle, \quad (7)$$

where $u_\alpha = \gamma_\alpha / \hbar \omega_\alpha$ is the displacement of bosons, $s = +1$ for spin up and -1 for spin down, and for simplicity we have dropped the molecular index n . Here, u_α , depending on the spin-boson coupling, is approximately equal to the Huang-Rhys factor S ($= \lambda / \hbar \omega$ with λ is the reorganization energy), which is commonly of the order ~ 1 in organic materials.[24] Throughout this work, we set the cutoff number of bosons to be 80 to ensure the calculation is convergent.

The second step is the *incoherent* hopping between molecules, whose rate could be derived in terms of the Fermi golden rule,[25]

$$\nu \approx \frac{\tau_{\text{if}}}{\hbar^2} |\langle f | H' | i \rangle|^2 = \frac{\tau_{\text{if}}}{\hbar^2} \text{Tr} \{ H' \rho_f H' \rho_i \}, \quad (8)$$

where $\tau_{\text{if}} \equiv 4\hbar^2 \sin^2[(E_f - E_i)t_d/2\hbar] / (E_f - E_i)^2 t_d$ with t_d being the decoherence time within which the hopping is coherent, and ρ_i ($|i\rangle$) and ρ_f ($|f\rangle$) are the initial and final density matrix (state) with the energy E_i and E_f , respectively, expressed in Eq. (5). t_d is a quantity determined approximately by the molecular structure relaxation, which gives it's at the order of 0.1ps.[11] It's noted that this treatment is qualitatively similar to the Franck-Condon principle,[21] which has been widely used in organic electronics as well as the spin-dependent exciton formation.[26] To determine the initial and final state in (8), we consider the following process. At a time when the process begins, a carrier with some spin s hops onto the n -th molecule, and the density matrix could be expressed as a direct product

$$\rho_n(t=0) = \varrho_n(s) \otimes \tilde{\varrho}_n, \quad (9)$$

where ϱ denotes the (2×2) spin density matrix of a carrier while $\tilde{\varrho}$ for bosons. Right at this moment, the interaction between the carrier and local bosonic modes is switched on, and then they become *entangled*. The system evolves following Eq. (6) till the carrier hops to the unoccupied n' -th molecule at time t_w , called waiting time, whose average value could be estimated by the mobility of carriers and bias voltage. For organic materials, $t_w \gg t_d$. After the hop, the carrier's spin and bosons on the n -th molecule disentangle. The spin state keeps unchanged because of spin-conserving, while the bosons will reorganize. An adiabatic elimination procedure technique is used for the spin state,[27] which gives the spin density matrix at the n' -th molecule as

$$\varrho_{n'}(s) = \text{Tr}_b \{ \rho_n(t_w) \}, \quad (10)$$

where the trace with subscript b is that over all bosonic degrees of freedom. For the reorganization of bosons, it depends on the relative ratio of the relaxation time of the bosonic environment (t_r), which is not explicitly known, and that of molecular structure ($\sim t_d$). In case $t_r \gg t_d$, the relaxation is negligible, so the bosonic density matrix becomes

$$\tilde{\varrho}_n = \text{Tr}_s \{ \rho_n(t_w) \}, \quad (11)$$

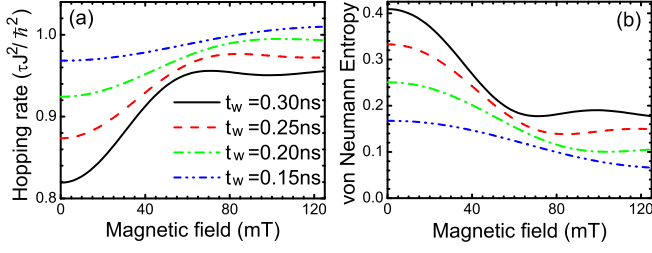


FIG. 1: Magnetic-field dependence of (a) the hopping rate ν (in unit of $\tau J^2 / \hbar^2$) between two molecules and (b) the von Neumann entropy for various waiting times t_w . $\gamma = 1.0\mu\text{eV}$ and $\hbar\omega = 2.0\mu\text{eV}$.

where the trace with subscript s is that over spin degree of freedom. But for $t_r \ll t_d$, the relaxation is complete, and $\tilde{\varrho}_n$ should return to its equilibrium state, in which all $u_\alpha = 0$. For an arbitrary ratio of t_r/t_d , we could introduce phenomenological parameters η_α depending on ω_α between 0 and 1. Thus, $\tilde{\varrho}_n$ in Eq. (7) should be that with all u_α replaced by $u_\alpha^* (\equiv \eta_\alpha u_\alpha)$. It will be seen later that the result is insensitive to the choice of η_α , *i.e.*, the relaxation of bosonic environments.

Now, the hopping rate could be derived directly from Eq. (8) as

$$\nu_{n \rightarrow n'} = \frac{\tau_{nn'} J_{nn'}^2}{\hbar^2} \text{Tr} \{ \tilde{\varrho}_n \varrho_{n'}(s) \rho_n(t_w) \}, \quad (12)$$

since it concerns only two molecules. Considering the random directions of a carrier's initial spin and its coupling with bosons, the hopping rate we calculate below will be averaged over all directions of the carrier's spin and that of applied magnetic field since the spin-boson coupling has been fixed along the z -direction.

Within the framework of perturbation theory, the interaction between different bosonic modes is not significant, so it is meaningful to investigate the system with an environment of a single bosonic mode. Hereafter we omit those molecular and boson's indexes if it would not create confusion. At first, the calculated hopping rate is shown in Fig. 1(a), from which we can see its strong dependence on external magnetic field as expected. We have set $\gamma = 1.0\mu\text{eV}$ and $\hbar\omega = 2.0\mu\text{eV}$, which correspond to an effective magnetic field $B_0 (\equiv 2\gamma^2 / \hbar\omega g\mu_B) = 8.6\text{mT}$ evaluated from Eq. (3). This field strength is similar with that used in HFI model for OMR[5] and extracted from muon experiment[28]. Accordingly, a saturation is reached for the magnetic field being 50 - 100mT depending on the waiting time t_w . It is clearly seen that the magnetic field dependence becomes stronger with a larger t_w . The slow waviness in those curves is due to the Rabi oscillation between spin states.

The observed magnetic field dependence originates from the incoherent hopping, which disentangle the spin and bosonic environment. To show it we calculated the von Neumann entropy[22], which is defined as

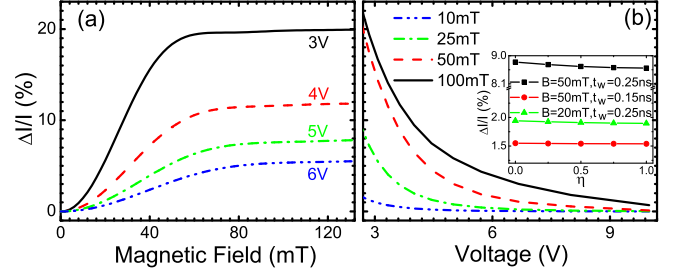


FIG. 2: (a) Magnetic field dependence of OMR under various bias voltages. (b) The dependence of OMR on the voltage under various magnetic fields. Inset shows the OMR is insensitive to η .

$\text{Tr}(\tilde{\varrho} \log_2 \tilde{\varrho})$. The result in Fig. 1(b) implies that the entanglement weakens the ability of a carrier hopping out of the environment. The external magnetic field changes the entanglement between the carrier and the bosonic environment, and then the magnetic field effect arises. This is the basic mechanism of OMR from our theory.

With the hopping rate between molecules in Eq. (12), we have the OMR as

$$\frac{\Delta I}{I} \equiv \frac{I(B) - I(0)}{I(0)} = \frac{\langle \nu(B) \rangle - \langle \nu(0) \rangle}{\langle \nu(0) \rangle}, \quad (13)$$

where $I(B)$ is the current depending on the magnetic field B , and $\langle \cdot \rangle$ is the average over samplings with a distribution of t_w here.[29] The average of t_w should be proportional to the inverse of bias voltage applied to a given device, which is expressed as $\langle t_w \rangle = L_D l / \mu V_b \xi$, with L_D being the thickness of device, l the intermolecular distance, μ the mobility of carriers, V_b the bias voltage, and ξ a factor introduced to account for the carrier's random hop. For example, we consider a typical OLED structure ITO (indium tin oxide)/NPB(N, N' -di-1-naphthyl- N, N' -diphenylbenzidine)(50 nm)/Alq₃ (tri-(8-hydroxyquinoline)-aluminum)(50nm)/Al (aluminum). The effective mobility of electrons in Alq₃ is taken as $\mu \approx 10^{-4}\text{cm}^2/\text{Vs}$, the average distance between molecules $l \approx 0.5\text{nm}$, and $\xi \approx 5$, so we have, *e.g.*, $\langle t_w \rangle \approx 0.25\text{ns}$ for $V_b = 4.0\text{V}$. Fig. 2(a) shows the OMR under different bias voltages. The basic line shape obtained here is in good agreement with a consensus based on experiments.[1, 5, 19, 30] Furthermore, we show the dependence of OMR on bias voltage under different magnetic field in Fig. 2(b). A decay following the voltage increase is found, which matches experimental observations.[19] For a small bias voltage, *e.g.*, $V_b < 2.0\text{V}$, the current is extremely small and the scattering between excitons becomes important, which is not included in this work, that might be the origin of positive OMR observed in experiments.[30] The η dependence of OMR is given in the inset, which verifies the choice of η has little influence.

Now we come to see the influence of a bosonic mode on the OMR. Fig. 3(a) shows the dependence of satu-

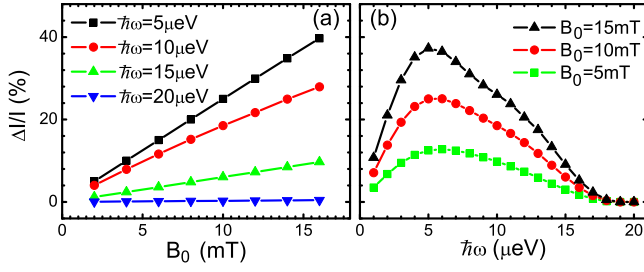


FIG. 3: OMR dependence on (a) the effective magnetic field B_0 and (b) the boson energy $\hbar\omega$ with $t_w = 0.25\text{ns}$.

rated $\Delta I/I$ on the spin-boson coupling γ , which is equivalent to the effective magnetic field B_0 , at $t_w = 0.25\text{ns}$. Obviously, OMR is found to be nearly proportional to B_0 in the range we calculated. Fig. 3(b) shows the frequency dependence of OMR. As expected, OMR approaches to vanishing when the frequency becomes large enough, where the bosonic mode is equivalent to an effective magnetic field, that is, the (classical) hyperfine field.[5, 10] From the perspective of entanglement, it's easy to understand the vanishing OMR since a classical field does not entangle with the carriers' spin. This also shows the quantum nature of local bosonic environments is *irreducible* for OMR.[31] It appears that the OMR peaks all reside at $\hbar\omega \approx 5.0\mu\text{eV}$, which is caused by setting the waiting time at a fixed value $t_w = 0.25\text{ns}$. Such phenomenon implies that bosonic modes of compatible energy with the waiting time contribute more to OMR.

Until now, we have discussed the environment of a single bosonic mode. In reality, a number of modes should contribute to OMR, and then the effective magnetic field B_0 we used in the one-mode case could be regarded as that defined in Eq. (3) within the perturbation theory. As has discussed, triplet-excitons play a basic role in the environment, so B_0 should be strongly dependent on the density of excitons that could be adjusted experimentally in many ways. Moreover, another important physical quantity to OMR is the boson energy $\hbar\omega$, which should depend on the constitution of the environment, related to characters of specific material, such as the mass of atoms and/or radicals in the molecule, electronic excitation energies. Due to the nonmonotonicity of OMR on $\hbar\omega$ as shown in Fig. 3(b), the discrepancy of isotope effect in different materials[6, 7] might be understood within the theory. It is also shown[17] experimentally that the OMR is strongly associated with the excitation energy by changing dopants.

In summary, we have proposed a theory based on the coupling between carriers' spin and a local bosonic environment. The entanglement is calculated to reveal the underlying mechanism of the anomalous OMR. The quantum nature of the environment is shown to be irreducible. The theory establishes the basic line shape of

OMR and its dependence on bias voltage in consistent with a consensus based on experiments. Triplet excitons are believed to contribute mostly to this environment, and relevant experiments are understood in accordance with the theory.

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